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Evgueni Barmatov<sup>a</sup>, Marina Barmatova<sup>a</sup>, Tamara Chenskaya<sup>b</sup> & Valery Shibaev<sup>a</sup>

<sup>a</sup> Chemistry Department, Moscow State University, 119899, Moscow, Russia

<sup>b</sup> Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70 Profsoyuznaya st., 117393, Moscow, Russia

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## New Principle of Molecular Design of LC Polymers by Covalent and Ionic Bonding of Side Groups

EVGUENI BARMATOV<sup>a</sup>, MARINA BARMATOVA<sup>a</sup>,  
TAMARA CHENSKAYA<sup>b</sup> and VALERY SHIBAEV<sup>a</sup>

<sup>a</sup>*Chemistry Department, Moscow State University 119899, Moscow, Russia and*

<sup>b</sup>*Institute of Synthetic Polymeric Materials, Russian Academy of Sciences 70  
Profsoyuznaya st., 117393 Moscow, Russia*

The combined principle to design comb-shaped LC polymers by covalent and ionic bonding of side groups with the main chain was suggested. The ionic complexes formed by a LC copolymers containing ~29 mol % of acrylic acid and octadecylamine were received. A study of phase behaviour of ionic complexes revealed the role that a low-molecular non-mesogenic component, attached through a non-covalent linkage to the main chain of the polymer, can play in the structure and properties of such ionic complexes.

**Keywords:** liquid crystals; polymers; ionic bonds; hydrogen bonds; phase diagrams; X-ray study

### INTRODUCTION

The conventional method of obtaining thermotropic side-chain liquid crystal (LC) polymers involves the chemical attachment of mesogenic groups to the main chain (Figure 1 a)<sup>[1,2]</sup>.

Recently, new methods for synthesis of LC side-chain polymers have been developed that are based on the use of specific non-covalent (electrostatic, donor-acceptor) interactions and intra- and intermolecular hydrogen bonds<sup>[3-21]</sup>. Ujiie, Iimura<sup>[6,7]</sup>, Bazuin<sup>[13,14]</sup>, Paleos, Skoulios<sup>[11,12]</sup> and Talroze<sup>[18]</sup> have proposed an alternative method for attachment of side groups to a polymer

chain involving self-organization of two moieties- a polymeric matrix (for example, polyacrylic acid) and a low-molecular amine (mesogenic or not mesogenic types) (Figure 1 b).

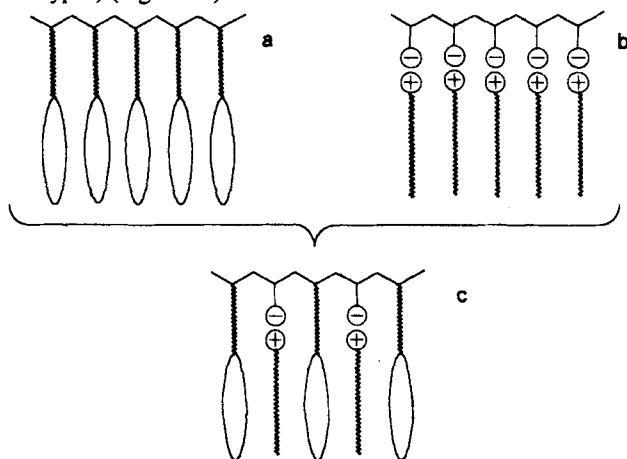
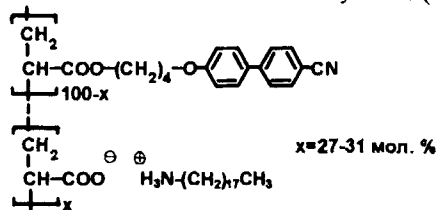


FIGURE 1. The different methods of molecular design of side-chain LC polymers.

Reaction between a polyacid and an amine proceeds, as a rule, through the formation of ionic complexes, which results in the occurrence of new structures showing a tendency towards thermotropic and/or lyotropic mesomorphism.

To-day, there is an ever-increasing interest in the study of LC polymeric systems based on the principle of molecular recognition and self-organization. In this context, it has been thought of interest to study the properties of side-chain LC polymers based on a mixed principle, that is, when the buildup of one portion of the macromolecule of a polymer involves covalent attachment of side groups, and of its another portion, electrostatic interaction (Figure 1c). The present paper is concerned with preparation of ionic complexes formed by an ionogenic LC copolymer containing ~29 mol % of acrylic acid and a low-molecular surfactant octadecylamine (ODA).



A study of phase diagrams of the system- ionogenic copolymer-amine has clarified the role that a low-molecular nonmesogenic component, attached through a non-covalent linkage to the main chain of the polymer, can play in the structure and thermostability of such ionic complexes.

Mixtures of ODA and a ionogenic copolymer of varied molecular weight are considered in this paper to see in what possible manner can the length of a polymer chain be the factor affecting properties of the complexes formed.

## EXPERIMENTAL

Copolymers<sup>[19-21]</sup> were obtained by radical copolymerization of monomers 4-(4-cyanobiphenyl-4'-yloxy)butyl acrylate and acrylic acid in absolute THF; AIBN was used an initiating agent. The concentration of acrylic acid in monomer mixture was 30 mol.%. The as-synthesized copolymers were purified by repeated reprecipitation from THF solutions by methanol.

The composition of copolymers was determined using methods of elemental analysis and infrared (IR) spectroscopy.

TABLE I. Molecular mass characteristics (GPC and combination of sedimentation and diffusion methods<sup>\*</sup>), composition and phase transitions of fractions of LC ionogenic copolymers.

N	$M_w \times 10^3$	$P_{SD}^*$	$M_w / M_n$	acrylic acid (mol %)	Phase transitions (°C)
1	12,60	100	1,53	27	g 41 N 112 I
2	7,32	59	1,29	28	g 39 N 101 I
3	3,21	25	1,26	31	g 32 N 76 I

The fractions of ionogenic copolymer obtained by fractional precipitation were used for preparation of complexes. Three fractions of ionogenic LC copolymers of different molecular weight and (what was important) of nearly the same composition were available for preparing mixtures. (Table I).

Complexes<sup>[20]</sup> of ionogenic copolymers and ODA ( $T_m=55-57^\circ\text{C}$ , Aldrich) were prepared by dissolving mechanical mixtures of these components taken in different proportion in chloroform; for further uses the complexes were dried in vacuum.

## RESULTS AND DISCUSSION

### Nature of non-covalent acid – amine interactions in mixtures

In the present work, IR spectroscopy was used for studying the hydrogen bonding in ionogenic copolymers and their mixtures with ODA.

Fraction 3 of the copolymer (Table I) was used in the study of interaction between ionogenic copolymer and amine. Mixtures containing 8.7, 14.5, 20.6, and 30 mol.% ODA were studied. Figure 2a shows the IR spectra the studied compounds. It is seen that the bands of the antisymmetric and symmetric  $\text{NH}_2$  stretching modes of free ODA (3340 and 3260  $\text{cm}^{-1}$ , respectively; curve 3) disappear completely from the spectrum of the mixture.

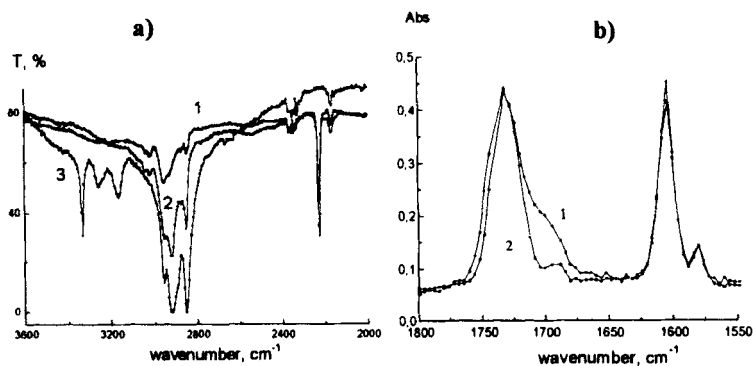
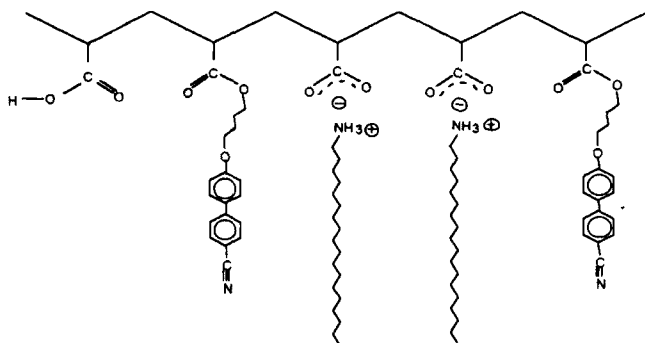


FIGURE 2 IR spectra of fraction 3 of ionogenic LC copolymer (curve 1), ODA (curve 3) and mixture containing 8.7 % ODA (curve 2).

The broad band at  $\sim 3200 \text{ cm}^{-1}$  due to the stretching mode  $\nu_{\text{OH}}$  of the H-bonded carboxyl group is observed to decrease in intensity. In the region of the stretching  $\nu_{\text{CO}}$  mode of the IR spectrum of the mixture, the intensity of the low-frequency and high-frequency wings of the complex  $\nu_{\text{CO}}$  band decreases with increasing amine concentration up to  $\sim 30\%$ ; further increase in concentration produces no change in the spectrum. The only band in this region at  $1730 \text{ cm}^{-1}$  is assigned to the stretching  $\nu_{\text{CO}}$  mode of the ester group. These data provide evidence for formation of an ionic complex  $-\text{COO}^{\ominus}\text{NH}_3^{\oplus}-\text{R}$  involving protonation of the  $\text{NH}_2$  groups of the amine by the carboxyl groups of the ionogenic copolymer. Indeed, in this case the  $\nu_{\text{NH}}$  bands are expected to disappear, and the bands of the  $\text{COOH}$  group, to be replaced by bands of the ion  $\text{COO}^{\ominus}$  in the range of  $1360\text{--}1450 \text{ cm}^{-1}$  (the strong overlapping the bands of bending CH modes hampers their identification).

Thus, the spectroscopic evidence lends support to the possible formation of ionic bonds between the acid group of the side-chain LC copolymer and octadecylamine. A schematic diagram representing the structure of a mixture

with partially substituted carboxyl groups of the ionogenic copolymer is given below.



### **Phase behavior of the mixtures**

Transition temperatures of the complexes were determined by methods of polarization microscopy and differential scanning calorimetry (DSC). The mixtures containing a nematic phase exhibit the characteristic marble texture. Formation of the  $S_A$ -phase was confirmed by observation of a fan-like or homeotropic texture as well as by the results of a X-ray diffraction analysis. The Bragg reflection and layer spacings were found to be  $5,1 \pm 0,1$  Å,  $d_{001} = 29,9 \pm 0,5$  Å,  $d_{002} = 14,9 \pm 0,3$  Å.

TABLE II. Wide angle Bragg reflections  $d_{110}$  and  $d_{200}$  and two dimensional rectangular of  $S_E$ -phase, and hexagonal lattice parameter of  $S_B$ -phase. Sample 1- mixture of fraction 3 and ODA, 29 mol %. Sample 2- mixture of fraction 1 and ODA, 27 mol %.

sample	Phase	$d_{110}$ , Å	$d_{200}$ , Å	$a$ , Å	$b$ , Å
1	$S_B$	4,16	-	4,8	-
2	$S_E$	4,10	3,71	7,42	4,92

For samples with an amine concentration  $>25$  mol.%, the DSC curves exhibit a low-temperature transition at  $49\text{--}54^\circ\text{C}$  with enthalpy  $\Delta H = 8\text{--}30$  J/g (depending on the amine concentration). The high melting heat is suggestive of the formation of ordered smectic phases in the mixtures studied. An analysis of the X-ray diffraction data shows that smectic  $S_B$ - and  $S_E$ -phases are observed in mixtures with amine concentration higher than 24 mol.%. Wide-angle Bragg reflections data and lattice parameters for the phases  $S_B$  and  $S_E$  are given in Table II. The unit cell parameters  $a$  and  $b$  are in

agreement with those reported in the literature<sup>[12]</sup> for the ordered phases formed in mixtures of polyacrylic acid with long-chain secondary amines.

### **Effect of the molecular weight of ionogenic LC copolymers on the phase behavior of mixtures**

We consider now in what a manner does the molecular weight of a polymer matrix affect the phase state of the complexes. To the best of our knowledge, no data concerned with this issue have been reported in the literature.

For an adequate analysis of the effect of polymer properties on the phase state of complexes, one will want to study copolymers samples over a wide range of degrees of polymerization and a rather narrow molecular-weight distribution. Accordingly the copolymers studied in the present work, had their molecular weights differing within a factor of four for a rather low polydispersion index of 1.26-1.53.

The phase diagrams for copolymer mixtures of different molecular weight are shown in Figure3. One will note a remarkable feature in the phase behavior of the mixtures, namely, disappearance of a nematic phase characteristic of the original ionogenic LC copolymer and formation of a  $S_A$ -phase at an ODA concentration of 5-14 mol %. Here the minimum concentration of aliphatic amine required for formation of a smectic phase decreases with increasing molecular weight of the copolymer. Such a behavior for complexes appears still more unexpected if one takes into account that the completion of a comb-like polymer is effected through attachment of aliphatic tails that lack mesogenic properties.

The reason for the unique behavior of complexes should be sought in the electrostatic nature of the bond between acid and primary amine. Presumably, the ionic pairs acid-amine self-organize into associates (multiplets) composed of two or more moieties<sup>[22]</sup>. The interchain associates play the role of physical cross-links that act to fix stiffly fragments of the polymeric chain between the network nodes. This, in turn, sets a limit to the freedom of movement of mesogenic and aliphatic side groups and promotes the occurrence of a translational order (a layer packing of side groups). Thus, the ionic clusters capable of lowering the entropy of the system, rather than the aliphatic long-chain side amine involved in the "completion" of the side-chain polymer, are mainly responsible for the smectic ordering at low ODA concentration.

The effect due to the aliphatic groups of octadecylamine is expected to appear at higher ODA concentrations when the effects of microphase segregating at a level of the side groups of the comb-like polymer come into play. At relatively high ODA concentrations (>24 mol %), ordered mesophases were observed to form.  $S_B$ -phase was formed in mixtures with degree of polymerization  $P_w=25-59$ , and  $S_E$ -phase, in those with  $P_w=100$ .



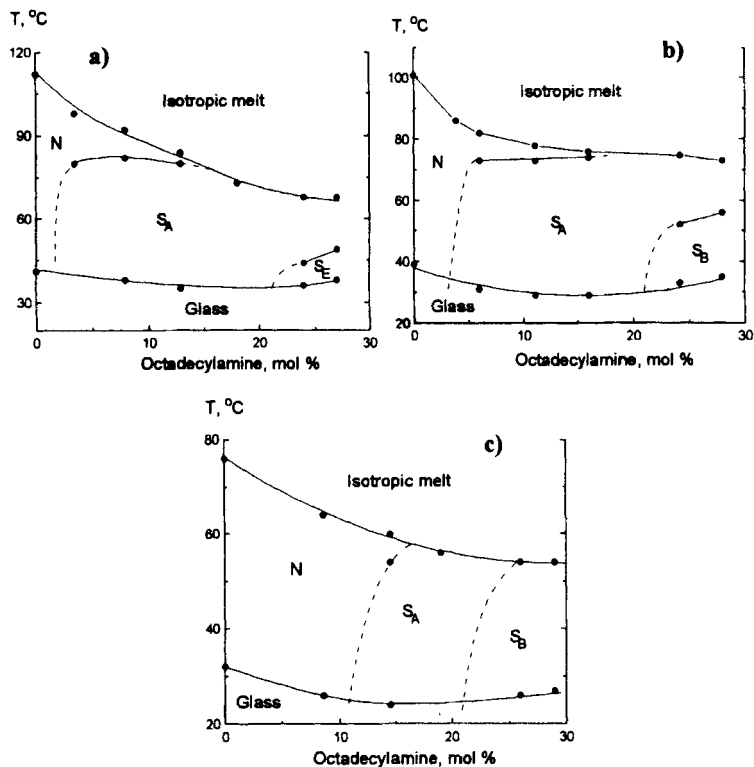


FIGURE 3 The phase diagrams of mixtures copolymer fractions with ODA: a) fraction 1; b) fraction 2; c) fraction 3 (Table I).

Presumably, the long methylene chains of octadecylamine that may be regarded as a microphase are responsible for the formation of ordered phases. However, a co-stacking of ODA molecules and mesogenic groups cannot be ruled out either.

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